

HYDROTHERMAL SYNTHESIS OF HEMATITE-RICH SPHERULES: IMPLICATIONS FOR DIAGENESIS AND HEMATITE SPHERULE FORMATION IN OUTCROPS AT MERIDIANI PLANUM, MARS. D. C. Golden¹, D. W. Ming², R. V. Morris², and T. G. Graff³. ¹ESCG-Hamilton Sundstrand, Houston, TX; ²Astromaterials Research and Exploration Science Directorate, NASA Johnson Space Center, Houston, TX (douglas.w.ming@nasa.gov); ³Arizona State University, Tempe, AZ.

Introduction: The Athena science payload onboard the Opportunity rover identified hematite-rich spherules (mean diameter of 4.2 ± 0.8 mm) embedded in outcrops and occurring as lag deposits at Meridiani Planum [1,2,3,4]. They have formed as diagenetic concretions from the rapid breakdown of pre-existing jarosite and other iron sulfates when chemically distinct groundwater passed through the sediments [4].

Diagenetic, Fe-cemented concretions found in the Jurassic Navajo Formation, Utah [5] and hematite-rich spherules found within sulfate-rich volcanic breccia on Mauna Kea volcano, Hawaii [6] are possible terrestrial analogues for Meridiani spherules. The Navajo Formation concretions form in porous quartz arenite from the dissolution of iron oxides by reducing fluids and subsequent Fe precipitation to form spherical Fe- and Si-rich concretions [5]. The Mauna Kea spherules form by hydrothermal, acid-sulfate alteration of basaltic tephra [6].

The formation of hematite-rich spherules with similar chemical, mineralogical, and morphological properties to the Meridiani spherules is rare on Earth, so little is known about their formation conditions. In this study, we have synthesized in the laboratory hematite-rich spherules that are analogous in nearly all respects to the Meridiani spherules.

Synthesis of Hematite-Rich Spherules: Fifteen mL each of 0.5 M MgSO_4 , 0.3M $\text{Al}_2(\text{SO}_4)_3$ and 0.5 M FeCl_3 solutions were transferred into 23 mL Teflon-lined steel reaction vessels. The vessels were sealed in ambient air and heated at 150°C for 4, 16, 24, or 72 hours and 200°C for 24 hours (forced hydrolysis). After cooling to room temperature, supernatants were decanted and reaction products were washed with distilled water to remove soluble salts and then freeze-dried. Mineralogical, chemical, and spectral properties of spherule precipitates were determined by X-ray diffraction analysis (XRD), electron microprobe analysis (EMPA), transmission electron microscopy (TEM), Moessbauer spectroscopy (MB), and thermal emission spectroscopy (TES).

Characterization of Hematite-Rich Spherules: Hydronium jarosite was the primary phase that formed after 4 h of forced hydrolysis at 150°C (Fig. 1a). Hematite-rich spherules formed along with hydronium jarosite after 16 h (Fig. 1b). After 24 hr, hematite, in the form of spherules, was the primary phase (Fig. 1c). Apparently, the process is hydrolysis of aqueous Fe^{3+} to form hydronium jarosite which in turn undergoes hydrolysis to form hematite. Although hematite can be

formed by a variety of processes [e.g., 7], the spherical morphology is rare in terrestrial environments. The unique spherical morphology apparently requires a forced hydrolysis process as suggested by [8] and observed under natural hydrothermal conditions on Mauna Kea volcano [6]. Although chloride anions appear to promote the spherical morphology [8], we have synthesized hematite spherules in the complete absence of chloride ions (data not shown). Jarosite and hematite are predicted in acid-sulfate weathering environments when solution pH is around 3 in oxidizing solutions [e.g., 9].

The hydronium jarosite has a pseudo-cubic morphology, which is typical for jarosite and the hematite occurs as spherules ranging from 3-5 μm to 5-20 μm in diameter in the shorter and longer duration experiments, respectively. Hydronium jarosite was identified by XRD and EMPA (absence of K and very low levels of Na). Hematite was identified by XRD, MB (Fig. 2) and TES (emissivity near 300, 450, and 550 cm^{-1} ; Fig. 3) for the 24h, 200°C product. Hematite spherules and hydronium jarosite contain approximating 4 wt % and 22 wt % water as inferred from EMPA totals less than 100%. This suggests that Fe-rich-spherules are hydrohematite. The high H_2O content is also evident in the TES spectra (Fig. 3).

The hematite-rich spherules exhibit a radial growth pattern consisting of fibrous hematite with the c-axis of particles aligned along the elongation direction of the hematite fibers (i.e., elongated along the [001] direction, TEM data not shown). A manifestation of this relationship is the absence of an emissivity minimum near 390 cm^{-1} (Fig. 3). The feature is also absent in hematite with a platy morphology [10].

Implications for Hematite Spherule Formation at Meridiani Planum:

The synthetic hematite spherules have many characteristics in common with the Meridiani Planum hematite spherules, including hematite mineralogy, spherical morphology, association with jarosite, and absence of a hematite emissivity minimum near 390 cm^{-1} , an important characteristic determined for Meridiani Planum hematite from Martian orbit [11]. There is however, one key difference: Meridiani hematite spherules are larger than our synthetic products. It is possible that we could form larger synthetic spherules, similar to the size of Meridiani spherules, through a synthetic system that would continuously supply the starting solution composition over time. The results of this study support the

conclusions of [4] that the spherules at Meridiani are diagenetic hematitic concretions that appear to have formed very rapidly under near isotropic fluid flow conditions by the breakdown of jarosite during basin recharge. However, our experiments and the Mauna Kea spherules [6] suggest that hydrothermal systems

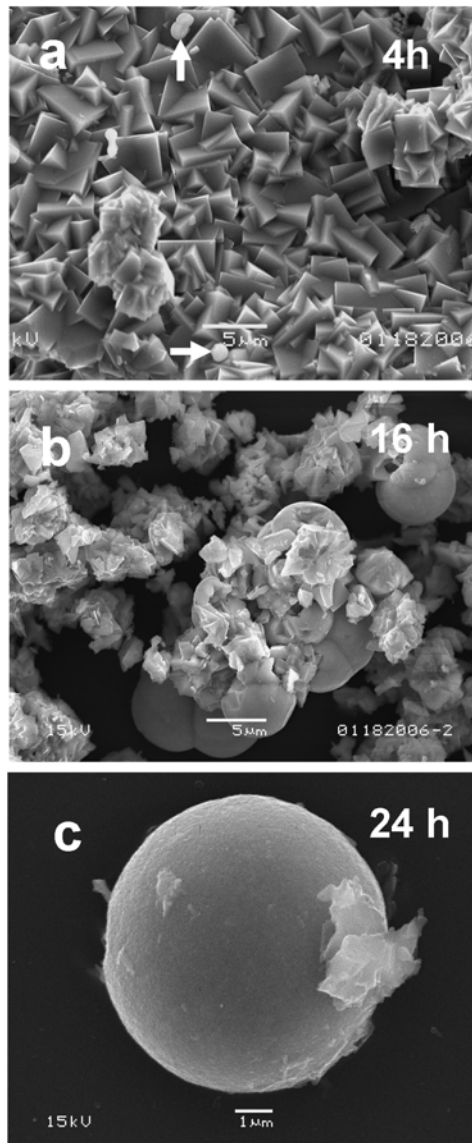


Figure 1: SEM images of synthetic hematite spherules and hydronium jarosite from forced hydrolysis of ferric solutions at 150°C: (a) hydronium jarosite and incipient hematite spherules (arrows) after 4 h ; (b) hydronium jarosite and hematite spherules after 16; and (c) a hematite spherule after 24 h duration.

may have been necessary for hematite spherule formation. We propose that the hematite spherules formed under mild hydrothermal conditions when warm solutions moved through the Meridiani

sediments, possibly from acid-sulfate groundwater heated by a near surface magmatic heat source.

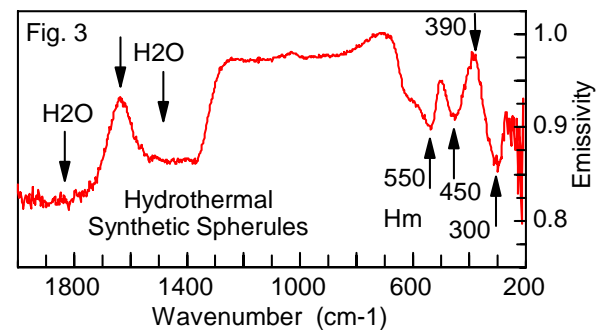
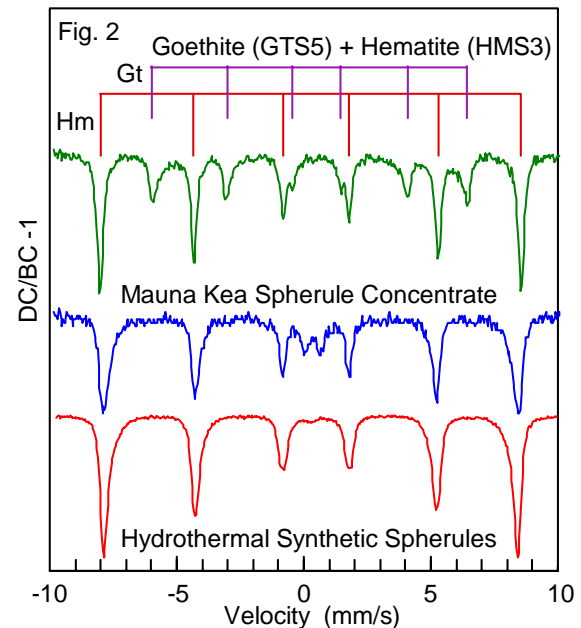


Figure 2. Mössbauer spectra for synthetic goethite (GTS5) and hematite (HMS3), hematite spherules from Mauna Kea volcano and hematite spherules synthesized in this study.

Figure 3. TES spectrum of hematite spherules synthesized in this study.

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